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Scaling and Universality in the Optics of Disordered Exciton Chains

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The joint probability distribution of exciton energies and transition dipole moments determines a variety of optical observables in disordered exciton systems. We demonstrate numerically that this distribution obeys a one-parameter scaling, originating from the fact that both the energy and the dipole moment are determined by the number of coherently bound molecules. A universal underlying distribution is found, which is identical for uncorrelated Gaussian disorder in the molecular transition energies or in the intermolecular transfer interactions. The universality breaks down for disorder in the transfer interactions resulting from variations in the molecular positions. We suggest the possibility to probe the joint distribution by means of single-molecule spectroscopy.

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Disorder is a ubiquitous phenomenon in many materials, with a strong effect on their observable properties. In practice, a rich variety of types of disorder occurs, while also the disorder strength varies widely. It is amazing that even though the detailed material properties generally are quite sensitive to disorder type and strength, the observables and their statistics often obey surprisingly universal scaling relations. One of the best known examples is the one-parameter scaling of the average conductance in disordered bulk conductors [1]. In fact, also the distribution and the fluctuations of this quantity exhibit universal behavior [2]. The same holds for the conductance of mesoscopic systems [3].

The conductance is determined by the system's collective charged excitations. In this Letter we will demonstrate that in disordered systems with collective neutral excitations (excitons), the optical properties exhibit universal scaling properties as well. In particular, we will consider the disordered Frenkel exciton chain, a model that describes a variety of quasi-one-dimensional optical materials, such as molecular aggregates [4–6], photosynthetic antenna systems [7,8], σ -conjugated polymers [9], and quantum wires [10] (see Ref. [11] for an overview). Disorder in these systems is induced by the inhomogeneity of the host (glass, polymer matrix, protein scaffold) or growth process (wires).

We study the joint probability distribution of transition energies and dipole moments and show that, for diagonal and off-diagonal Gaussian white noise, this distribution obeys a universal one-parameter scaling in the Lifshits tail below the bare band edge, which is the energy region that dominates the optical response. The scaling behavior uncovered by us puts a common origin under scaling relations reported in the literature for the width and shift of the absorption spectrum [5], radiative rate enhancement [5,6], and the fluorescence Stokes shift [6].

The joint distribution introduced here reads

$$\mathcal{G}(\varepsilon, \mu) = \frac{1}{N} \left\langle \sum_{\nu=1}^N \delta(\varepsilon - \varepsilon_{\nu}) \delta(\mu - \mu_{\nu}) \right\rangle, \quad (1)$$

where ν labels the eigenstates of the system, ε_{ν} and μ_{ν} denote their energies and dipoles to the ground state, and $\langle \dots \rangle$ indicates the average over realizations of the disorder. Several important optical quantities directly follow from this distribution. Thus, the ensemble averaged linear absorption spectrum reads $\mathcal{A}(\varepsilon) = \int d\mu \mu^2 \mathcal{G}(\varepsilon, \mu)$. If the exciton population thermalizes fast on the emission time scale, the fluorescence line shape can be written $I(\varepsilon) = \exp(-\varepsilon/k_B T) \int d\mu \mu^2 \mathcal{G}(\varepsilon, \mu)$, where T is the temperature and k_B denotes Boltzmann's constant. We recently showed that $\mathcal{G}(\varepsilon, \mu)$ naturally emerges in models of bistable optical response of exciton systems [12]. Knowledge of $\mathcal{G}(\varepsilon, \mu)$ also allows one to calculate the density of states (DOS), $\mathcal{D}(\varepsilon) = \int d\mu \mathcal{G}(\varepsilon, \mu)$, and the distribution of the transition dipole moment, $\mathcal{M}(\mu) = \int d\varepsilon \mathcal{G}(\varepsilon, \mu)$.

We consider a Frenkel exciton chain of N sites ("molecules"), labeled $n = 1, \dots, N$, each with a single dipole allowed optical transition with energy E_n . The transition dipoles of all sites are assumed to be equal in magnitude and orientation; this magnitude is chosen as the unit of dipole moment. Between sites excitation transfer interactions J_{nm} exist. The corresponding Hamiltonian reads

$$H = \sum_{n=1}^N E_n |n\rangle \langle n| + \sum_{n,m \neq n}^N J_{nm} |n\rangle \langle m|, \quad (2)$$

where $|n\rangle$ denotes the state in which site n is excited and all other sites are in the ground state.

We consider three different cases of the above model, which differ predominantly in the type of disorder. In case (i), diagonal disorder, we take the E_n as uncorrelated Gaussian random variables with zero mean (i.e., we take the average excitation energy of a single site as the origin of the energy scale) and standard deviation σ_E . The inter-

actions will be taken nonrandom as $J_{nm} = -1/|n - m|^3$, which are the long-range (LR) dipole-dipole interactions. The magnitude of the nearest-neighbor (NN) interaction is chosen as the energy unit.

In cases (ii), and (iii), off-diagonal disorder, all molecular transition energies are equal and set to zero. In case (ii), we consider only NN interactions and take these as uncorrelated Gaussian random variables with mean -1 and standard deviation σ_J . In case (iii), the interaction disorder is modeled by random displacements of the sites. The position of site n is given by $n + \xi_n$, with ξ_n being a dimensionless random variable [13]. These displacements translate into random couplings $J_{nm} = -1/|n - m + \xi_n - \xi_m|^3$. We take the ξ_n independently of each other from a Gaussian distribution with zero mean and standard deviation σ_ξ . This model leads to non-Gaussian and correlated disorder in the intermolecular interactions [14].

The exciton wave functions are localized by the disorder. The optically dominant states occur mostly in the DOS tail, below the lower bare band edge ε_b ($\varepsilon_b = -2$ and $\varepsilon_b = -2.404$ for NN and LR dipolar interactions, respectively). They are characterized by s -like wave functions that have no nodes on the main part of their localization segments [15]. The disorder imposes a typical localization size, N^* , for these states, which determines the typical transition dipole moment $\mu^* \propto \sqrt{N^*}$ (see, e.g., Ref. [5]). Thus, the oscillator strength $\mu^{*2} \propto N^*$, a property that is referred to as superradiant enhancement. N^* is also often referred to as the number of coherently bound molecules. Furthermore, in the DOS tail the disorder imposes a typical energy scale: $E^* \propto 1/\sqrt{N^*}$, where the factor of $1/\sqrt{N^*}$ arises from the phenomenon of exchange narrowing [16]. The quantity E^* determines the width of the absorption band and its shift from ε_b . The above suggests that the disorder scaling of both the energy and the transition dipole moment are dictated by N^* . As it is well established, N^* only depends on the disorder strength σ_i according to powerlaws (see, e.g., Refs. [5,14]), either σ_i or N^* may be chosen as scaling parameter. Thus, $E_i^* \sim \sigma_i^{\alpha_i}$ and $\mu_i^* \sim \sigma_i^{\gamma_i}$ for appropriate α_i and γ_i .

The above arguments lead to the conjecture that if energies and dipoles are measured on the scale of E^* and μ^* , respectively, the joint distribution $\mathcal{G}(\varepsilon, \mu)$ may become invariant after introducing the scale transformations

$$\tilde{\varepsilon} = \frac{\varepsilon - \varepsilon_b + a_i \sigma_i^{\alpha_i}}{b_i \sigma_i^{\alpha_i}}, \quad \tilde{\mu} = \frac{\mu}{c_i \sigma_i^{\gamma_i}}, \quad (3)$$

where $a_i \sigma_i^{\alpha_i}$ is the disorder induced energy shift of the exciton band edge and $b_i \sigma_i^{\alpha_i}$ is the disorder induced (inhomogeneous) broadening. The parameters a_i , b_i and c_i are constants that depend on the type of disorder. If our scaling conjecture holds, the joint distribution should obey $\mathcal{G}(\varepsilon, \mu) = k \tilde{\mathcal{G}}(\tilde{\varepsilon}, \tilde{\mu})$, where $k = (b_i c_i)^{-1} \sigma_i^{-(\alpha_i + \gamma_i)}$ is the Jacobian of the transformation (3), which ensures normalization, and $\tilde{\mathcal{G}}(\tilde{\varepsilon}, \tilde{\mu})$ is a universal function that does not depend on the strength and type of the disorder.

We have investigated the validity of our scaling conjecture (3) by calculating $\mathcal{G}(\varepsilon, \mu)$ for the cases (i)–(iii) with various disorder strengths. To this end, we numerically sampled disorder realizations and diagonalized the Hamiltonian matrix $H_{nm} = \delta_{nm} E_n + (1 - \delta_{nm}) J_{nm}$ to obtain the exciton eigenenergies ε_ν and wave functions φ_ν (chosen to be real). The transition dipoles read $\mu_\nu = \sum_n \varphi_{\nu n}$. We typically sampled a few hundred thousand disorder realizations for chains of $N = 500$ sites to compute $\mathcal{G}(\varepsilon, \mu)$ according to Eq. (1).

We first present our results for the case of diagonal disorder with long-range interactions, case (i). We only plot the distribution for $\mu \geq 0$, because $\mathcal{G}(\varepsilon, \mu) = \mathcal{G}(\varepsilon, -\mu)$. A typical example of the distribution function $\mathcal{G}(\varepsilon, \mu)$, obtained for an ensemble of chains with diagonal disorder strength $\sigma_E = 0.4$, is depicted in Fig. 1 (panel a), together with the DOS $\mathcal{D}(\varepsilon)$ (panel b), the absorption spectrum $\mathcal{A}(\varepsilon)$ (panel c), and the probability density of the dimensionless transition dipole moment $\mathcal{M}(\mu)$ (panel d). Obviously, the joint distribution in Fig. 1(a) gives considerably more insight into the nature of the various states than the DOS or the distribution of dipole moment. The well-known low-energy peak that exists in $\mathcal{D}(\varepsilon)$ for one-dimensional systems (panel b) is spread out in the second dimension, revealing that most of the oscillator strength per exciton state indeed occurs in this energy region and that the variation in this strength is quite large. The distribution of the transition dipole moment $\mathcal{M}(\mu)$ (panel d) reveals a strong peak at $\mu = 0$, which from panel a is seen to originate from the exciton states that lie within the bare band, while the much less intense features at finite values of μ arise from states in the Lifshits tail, below the bare band edge at $\varepsilon_b = -2.404$.

Figure 2, upper row, shows the distribution $\mathcal{G}(\varepsilon, \mu)$ for three values of σ_E . We restrict ourselves to the energy region below ε_b , where the optically dominant states occur.

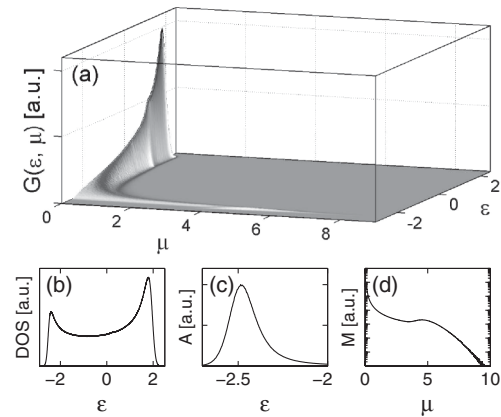


FIG. 1. (a) The joint probability distribution $\mathcal{G}(\varepsilon, \mu)$ for case (i) with disorder of strength $\sigma_E = 0.4$ obtained by simulating Eq. (1). (b) The density of states $\mathcal{D}(\varepsilon) = \int d\mu \mathcal{G}(\varepsilon, \mu)$. (c) The absorption spectrum $\mathcal{A}(\varepsilon) = \int d\mu \mu^2 \mathcal{G}(\varepsilon, \mu)$. (d) The distribution $\mathcal{M}(\mu) = \int d\varepsilon \mathcal{G}(\varepsilon, \mu)$ of the dimensionless transition dipole moment μ .

At first sight, the distributions look very different. With increasing value of σ_E , the distribution shifts down and broadens along the ε direction and also shifts towards lower dipole moment. These trends are consistent with the fact that increasing the disorder strength leads to a decrease of the typical localization size N^* , which, in turn, results in increasing E^* and reducing μ^* .

The lower row in Fig. 2 shows the same distributions, after applying the scale transformation Eq. (3), with $a_E = 0.51$, $b_E = 1.11$, $c_E = 2.85$, $\alpha_E = 1.44$, and $\gamma_E = -0.43$. It is clear that after rescaling the distributions indeed are (almost) the same over a large range of the disorder parameter σ_E , thus confirming the scaling conjecture. The constants a_E , b_E , c_E , α_E , and γ_E were determined by a fit procedure that searches for an optimal agreement between the rescaled distributions. Here, it should be realized that already known scaling relations narrow the range of possible values, in particular, for the powers α_E and γ_E . The power $\alpha_E = 1.44$ deviates slightly from the values 1.34 and 1.35 that were obtained for the width and the shift of the absorption band in previous work [5]. Using the relation $\mu^* \propto \sqrt{N^*}$, the power $\gamma_E = -0.43$ may be compared with the scaling of the typical localization length N^* . For the latter, previous studies yielded $N^* \propto \sigma_E^{-0.74}$ [5] and $N^* \propto \sigma_E^{-0.8}$ [15] (using different definitions for N^*), which translates into values of γ_E of -0.37 and -0.4 , in good agreement with our findings. We also note that the values of $\alpha_E = 1.44$ and $\gamma_E = -0.43$ comply well with the exchange narrowing argument ($E^* \propto \sigma_E/\sqrt{N^*}$), which implies that $\alpha_E = 1 - \gamma_E$. All this confirms that N^* indeed underlies the one-parameter scaling.

We next turn to case (ii), NN interactions with Gaussian disorder. Figure 3, two upper rows, presents the results for three values of the disorder strength σ_J , before and after scaling. The scaling coefficients that were used to obtain

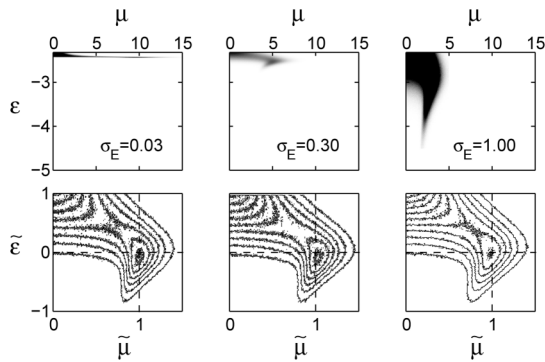


FIG. 2. Upper row: Gray-scale representation of the joint probability distribution $\mathcal{G}(\varepsilon, \mu)$ near the lower band edge, calculated for case (i), i.e., long-range interactions and diagonal disorder, using three different disorder strengths σ_E given in the panels. Lower row: Contour plots of the same distributions, after applying the transformations (3) with constants given in the text. After rescaling, the peak of the distribution lies close to the point $(\tilde{\varepsilon}, \tilde{\mu}) = (0, 1)$. Contours are given at 0.9, 0.75, 0.6, 0.45, 0.3, and 0.15 of the peak value.

the second row from the first one, are $a_J = 0.95$, $b_J = 2.55$, $c_J = 1.8$, $\alpha_J = 1.26$, and $\gamma_J = -0.325$. Like in case (i), we observe that the low-energy region of the distribution $\mathcal{G}(\varepsilon, \mu)$ also in this case seems to derive from a universal function. Again the powers α_J and γ_J obey $\alpha_J \approx 1 - \gamma_J$, confirming the central role of N^* .

Figures 2 and 3 show a strong similarity of the underlying distributions for cases (i) and (ii). We have tested this apparent universality more quantitatively by taking the distribution $\tilde{\mathcal{G}}(\tilde{\varepsilon}, \tilde{\mu})$ obtained from case (i) with $\sigma_E = 1$ as reference function and using the inverse of the scale transformations found above for case (ii) in order to derive the distributions $\mathcal{G}(\varepsilon, \mu)$ for $\sigma_J = 0.03$, 0.1, and 0.3. We then calculated the absorption spectra for these three values of σ_J according to the expression $\mathcal{A}(\varepsilon) = \int d\mu \mu^2 \mathcal{G}(\varepsilon, \mu)$ and compared these to the absorption spectra calculated directly by simulating the sum-over-states in $\mathcal{A}(\varepsilon) = (1/N) \langle \sum_\nu \mu_\nu^2 \delta(\varepsilon - \varepsilon_\nu) \rangle$. The comparison, presented in Fig. 3, lower row, shows an almost perfect agreement between both ways of obtaining the spectra, suggesting that the underlying distribution (in the optically important energy region) indeed is the same for both cases. Since case (i) includes all LR dipolar interactions and case (ii) only has NN interactions, this also strongly suggests that shorter-range (multipolar) corrections to the LR interactions would not affect the universality.

It turns out that case (iii), where the interaction disorder results from positional disorder, does not fall in this universality class. We have found that, first of all, in order to generate a reasonably universal distribution within this

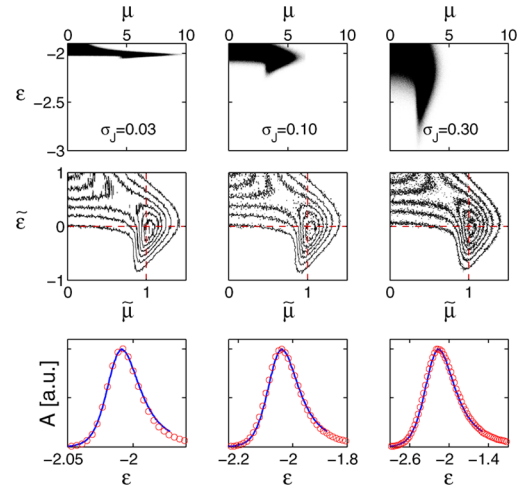


FIG. 3 (color online). Upper two rows: Same as in Fig. 2, only calculated for case (ii), i.e., for Gaussian uncorrelated random NN interactions, using three different values of the disorder strength σ_J . Lower row: Absorption spectra calculated for the same model parameters. The circles show the results obtained through direct simulation of the spectra using a sum-over-states expression, while the solid line is obtained from $\mathcal{A}(\varepsilon) = \int d\mu \mu^2 \mathcal{G}(\varepsilon, \mu)$ and using the scale transformations to translate the $\tilde{\mathcal{G}}(\tilde{\varepsilon}, \tilde{\mu})$ distribution obtained for case (i) with $\sigma_E = 1$ to the ones applicable to case (ii) (see text).

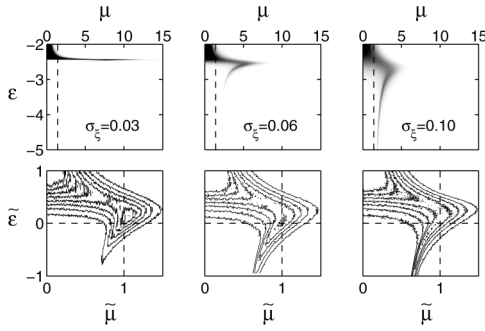


FIG. 4. Same as in Fig. 2, only calculated for case (iii), i.e., LR dipolar interaction disorder deriving from positional randomness. Note that the low-energy tail of $G(\varepsilon, \mu)$ tends to $\sqrt{2}$ (dashed line), reflecting the occurrence of dimer states. In the lower row, contours are drawn at 0.8, 0.6, 0.4, and 0.2 times the peak value of the distribution.

case, an additional exponent needs to be introduced in Eq. (3): the shift $a_\xi \sigma_\xi^{\alpha_\xi}$ should be replaced by $a_\xi \sigma_\xi^{\beta_\xi}$. Figure 4 shows the results of simulating $G(\varepsilon, \mu)$ for three values of σ_ξ and our best attempt at rescaling the distributions with this modified transformation (using $a_\xi = 61$, $b_\xi = 46$, $c_\xi = 0.52$, $\alpha_\xi = 2.06$, $\beta_\xi = 2.7$, and $\gamma_\xi = -0.8$). The distributions obtained after rescaling do bear a resemblance to each other, but we also observe that the “beak” type structure on the lowest-energy side gets more pronounced with increasing σ_ξ . Moreover, we see that these rescaled distributions differ significantly from those obtained in cases (i) and (ii), in particular, again, in the beak structure. The underlying reason is that this disorder model leads to the occurrence of a new type of states that do not exist in the other models, namely, local dimer states. These states originate from relatively large fluctuations in the monomer positions, which can strongly reduce the distance between neighboring monomers, thus enhancing the dipolar interactions and leading to effective dimers in the chain at low energies. The dimer tail in $G(\varepsilon, \mu)$ is not scale invariant and can be considered as a signature of positional disorder; we also expect this tail to be sensitive to multipolar corrections to the interactions.

To summarize, we have introduced the joint distribution function $G(\varepsilon, \mu)$ of the transition energy and dipole moment of states as a new quantity governing the optical properties of disordered systems. We have shown that for one-dimensional exciton systems with uncorrelated diagonal or off-diagonal Gaussian disorder the optically relevant part of this distribution derives from one universal underlying function by one-parameter scaling. For positional disorder this universality breaks down. We stress that $G(\varepsilon, \mu)$ contains all stochastic information relevant to the system’s optical response. While ensemble spectra, such as the absorption spectrum, only contain this information in a convoluted way, direct measurement of $G(\varepsilon, \mu)$ could give more insight into issues such as the disorder mechanism. We believe that $G(\varepsilon, \mu)$ may be

measured using single-molecule fluorescence excitation spectroscopy, where individual excitonic peaks can be resolved [8,17], and single-molecule pump-probe spectroscopy, which in principle allows measuring the energy and lifetime (dipole) of exciton transitions [18,19]. Such experimental studies could reveal deviations from a Gaussian uncorrelated nature of the disorder and possible deviation from pure one dimensionality.

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